FABRICATION OF SPHERICAL AND IRREGULARLY SHAPED POWDERS OF Li AND Ba TITANATES FROM TITANIUM TETRACHLORIDE BY INORGANIC SOL-GEL PROCESS*

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We report preparation procedures for some lithium and barium titanate compounds. The procedures utilize inexpensive, commercial $TiCl_4$ in an aqueous HCl solution. The main preparation steps consist of chloride elimination by distillation with nitric acid, addition of hydroxides of Li (or Ba), evaporation of sols to dry powders, and thermal treatment to titanates. Thermal and X-ray analyses indicate that the formation temperatures are lower than the corresponding temperatures necessary for conventional solid-state reactions. These temperatures can be further decreased by addition of ascorbic acid during formation of Ti nitrate sols. Spherical powders (with particle diameters of <100μm) are obtained by solvent extraction of water from sol drops emulsified in 2-ethylheksanol-1. Final correction of the composition of the spherical powders is carried out by an impregnation process.

1. INTRODUCTION

Lithium and barium titanates have been extensively studied as materials for advanced technologies, such as superconductors ($LiTi_2O_4$), tritium breeders for fusion reactors (Li_2TiO_3), cathodes for Li-batteries ($Li_4Ti_5O_{12}$), and, e.g., capacitors ($BaTiO_3$). All of these compounds were first fabricated by solid-state reaction of oxides and/or metallic salts. Wet processing, especially sol-gel procedures, has been applied successfully to synthesis some of them. Advantages of wet techniques derive from precise compositional control and homogeneity on a molecular scale. After the

pioneering work of Mazdyiasni and coworkers[1] on synthesis of $BaTiO_3$, many papers have described sol-gel processes for titanate formation. The precursors have generally been various organometallic compounds for Ba or Li and Ti substrates for the Ti.[2-16] Reports have noted that sol-gel-derived powders can allow for decreased sintering temperatures. Problems associated with these methods include the high cost of substrates[5] and deleterious formation of $BaCO_3$ during thermal conversion of gels.[7-10,13,14] Similar problems have been observed when Ba-Ti organic complexes are thermally decomposed to $BaTiO_3$.[6,9,11] Relatively few recent papers have reported sol-gel synthesis of Li titanates (Li_2TiO_3[15] and $Li_4Ti_5O_{12}$[16]).

A key question in processing titantes[17-31] is the source of titania. Titania products are commonly derived from inexpensive commercial $TiCl_4$.[5] Wet processing of commercial anhydrous $TiCl_4$ with ethanol has been described[5,26] Another possibility is dissolution of $TiCl_4$ in water to form $TiOCl_2$.[5,18,30,31]

We have developed[19,20] a process in which TiO_2 particles with diameters of <100 μm were produced by a sol-gel process: a titania sol, $TiO(OH)_{1.3}Cl_{0.3}$, was prepared by extraction of chlorides from a solution obtained by dissolving $TiCl_4$ in concentrated HCl. We used this sol to produce Li_2TiO_3, and observed a negative influence of chlorides due to presence of the strongly electropositive Li ions.[27,28] We therefore settled upon use of dechlorination with nitric acid.[27,28] Li_2TiO_3 could then be synthesized at a temperature 400°C lower than that need when chloride sols were used. This method differs from published processes[17,22,30] that involve precipitation from an aqueous $TiOCl_2$ solution with ammonia.

The goal of this work was to use concentrated Ti-O nitrate sols to produce irregularly shaped and spherical particles of Li and Ba titanates. Moreover, a strong complexing agent (ascorbic acid, ASC) was used to stabilize various sols. This proprietary procedure (IChTJ) has been patented[25] and successfully applied to synthesis of materials such as hydroxyapatite,[29] $LiMn_2O_4$,[32] and $LiNi_xCo_{1-x}O_2$.[33]

2. EXPERIMENTAL DETAILS

A flowchart of the preparation procedures is shown in Fig. 1. Commercial $TiCl_4$ was introduced via pumping into concentrated HCl. Excess HCl was exhausted, resulting in a solution of molar ratio Cl:Ti ≈ 3 and high Ti concentration (≈4 M). The main preparation steps consisted of chloride elimination by distillation with nitric acid (in Rotavapor equipment (Büchi, Switzerland)), addition of hydroxides of Li (or Ba), evaporation of sols to dry powders, grinding, and thermal treatment to titanates. Spherical gelled particles with diameters of <100 μm were produced by the IChTJ variant[19,20] of the sol-gel process. In this process, powders were synthesized

by extraction of H_2O from inorganic hydroxyl sol emulsion drops in ethylhexanol (EH), following by thermal treatment. However, in this process, the Li:Ti molar ratio decreased markedly because of extraction of Li or Ba nitrate along with water. To prepare a stoichiometric gel, we added an impregnation step:[28] the required quantity of MeOH solutions was introduced into gel microspheres that were placed into the Rotavapor.

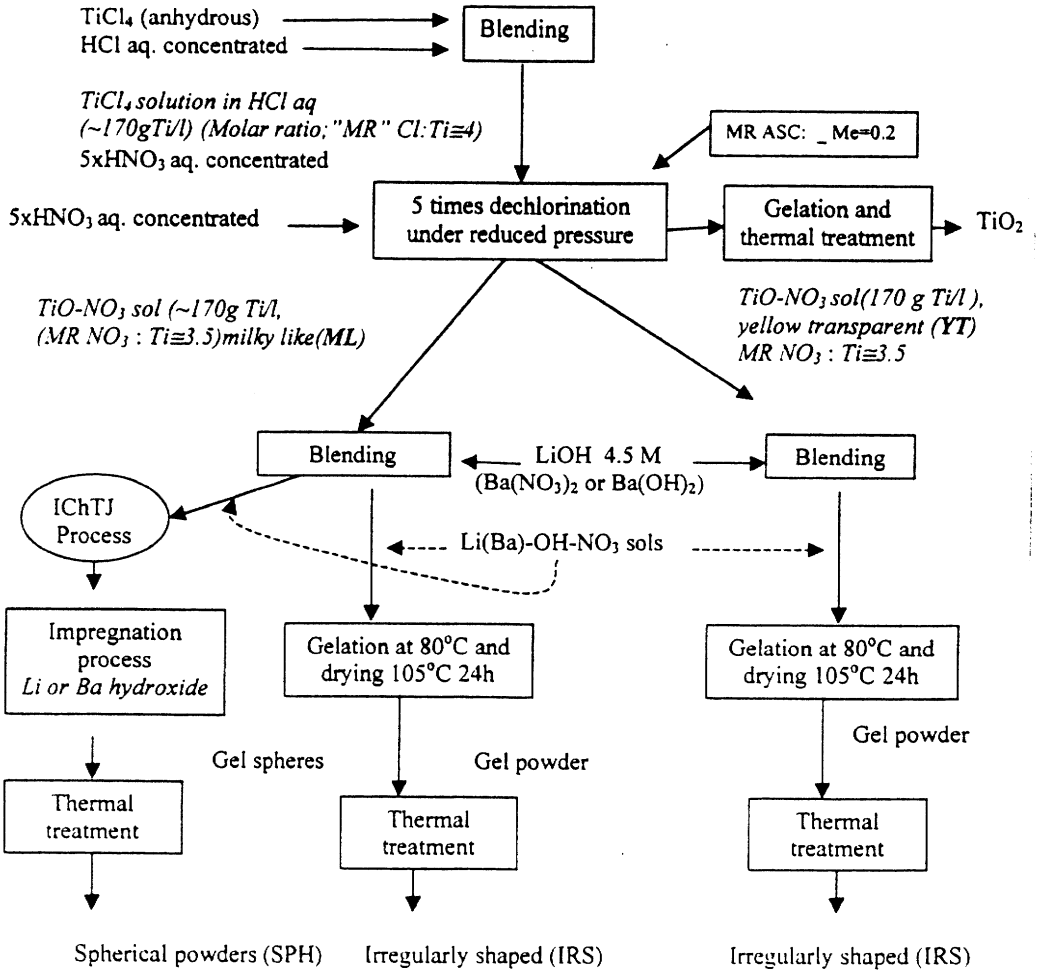

FIGURE 1
Flowchart for preparation of irregularly shaped and spherical powders of Li or Ba titanates by sol-gel processing

Thermal treatments were conducted in air. Gels and final powders were characterized by: (1) thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in a Hungarian MOM Derivatograph, for which the sample weight = 200 mg, heating rate = 10°C/min., atmosphere = air, and reference material = Al_2O_3; (2) X-ray diffraction (XRD) by Cu Kα radiation in a Philips Diffraction System; and (3) scanning electron microscopy (SEM) in a Zeiss DSM 942.

3. RESULTS AND DISCUSSION

The processing procedures followed are summarized in Fig. 1. To avoid the sol concentration step used in Ref. 19, we carried out distillation after adding every portion of HNO_3 to obtain volumes identical to the starting volume of $TiCl_4$ solutions. We found that complete removal of the Cl^- from each $TiCl_4$ solution was relatively easily accomplished, and required only five distillation steps. In comparison, e.g., for processing $SnCl_4$ to $SnCl_{3.5}$, 13 distillation steps are required for dechlorination (Fig. 2).[19] Formation of stable polymeric colloidal titanic acid is presumed to participate with bidentate nitrate ions in their formation and repulsion of Cl^- from the colloidal particles. We observed that if distillation temperature (due to higher pressure) were higher (routinely we used 70°C), a white milky solution became unstable and exhibited a tendency to agglomerate. The composition of the final sol was $\approx TiO\text{-}3.5NO_3$ due to distillation of HNO_3.

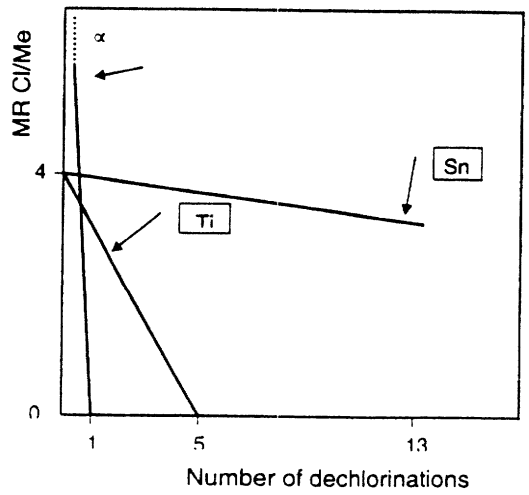

FIGURE 2
Ratio of Cl– to metal ions vs. distillation steps for Ti and Sn sols

In the initial processing, in which the distillation temperature was 70°C, a white milky appearing solution formed; it exhibited a tendency to agglomerate and form sediments. We surmised that formation of stable colloidal titanic acid induced repulsion of Cl^- from the colloidal particles. Following our earlier experience,[25] we added ascorbic acid (ASC) before the dechlorination step to prevent precipitation. The resulting sols were transparent, pale yellow, and stable. During the dechlorination steps, we observed decomposition and vigorous evolution of gas due to oxidation of the ASC by the nitrates. For the Li titanates, the additional processing steps for introducing the cations were as described previously.[28]

Some difficulties were observed if Ba^{2+} compounds were added because of limited solubility of $Ba(NO_3)_2$. As a consequence, we chose to dilute the $Ba(NO_3)_2$ solutions used. When $Ba(OH)_2$, was used, heating to near boiling was necessary to maintain a high concentration of the components.

3.1. Li_2TiO_3

Preparation of spherical particles of Li_2TiO_3 has been described.[28] As we reported, of direct importance to fusion reactors, the sol-gel-derived materials exhibited better tritium release than those produced by solid-state methods. Thermal analyses of the irregularly shaped gel powders of Li_2TiO_3 and $LiNO_3$ are shown Fig. 3. The endothermic event at ≈250°C can be attributed to melting of Li nitrate. No exothermic events were observed, which indicates that the gels did not contain organics. Figure 3 also contains thermal analyses of a gel of Li_2TiO_3 in which ASC was introduced by impregnation. Strong exotherms associated with its decomposition were observed. This result confirms our supposition that all of the added ASC decomposed in the preparation step. For all compositions, decomposition of nitrates was noted at ≈500°C as sharp decreases in weight, accompanied by a distinct endothermic event. However, for the gels prepared with addition of ASC (denoted ASCD), all of the ASC decomposed during dechlorination and weight loss started at ≈300°C. This lower temperature can be attributed to evolution of OH groups formed in reaction with ASC:

$$TiO(OH)_a\text{-}3.5NO_3\text{-}H_2O + ASC \Rightarrow TiO(OH)_{a+x}\text{-}(3.5\text{-}y)NO_3\text{-}H_2O\text{-}CO_2\,.$$

Weight stabilization for both gels occurred at 600°C. XRD patterns of final products from both types of gels materials were similar and represented crystalline Li_2TiO_3 (Fig. 4).

3.2. $Li_4Ti_5O_{12}$

Thermal decompositions of 4Li-5Ti chloride (before dechlorination) and nitrate gels are shown in Fig. 5. The TGA and DTA traces were roughly similar for those of the titanates from Fig. 3. The final decomposition step connected with formation of $Li_4Ti_5O_{12}$ at ≈600°C seemed to have been shifted to slightly lower temperatures for the ASCD gel. Samples of heated at 900°C consisted of crystalline $Li_4Ti_5O_{12}$ (Fig. 6). In contrast, for chloride gel (as for Li_2TiO_3),[28] the final decomposition step was observed ≈1100°C. At 900°C, the powder consisted of a mixture of TiO_2 (rutile and anstase), LiCl, and various Li titanates.

The results confirm the effectiveness of the dechlorination procedure. Electrochemical tests indicated that synthesized material has shown a very fast kinetics toward the Li^+ intercalation-deintercalation reaction and high thermodynamic reversibility. These properties positively affected testing of the material, which underwent >100 cycles at high current density.

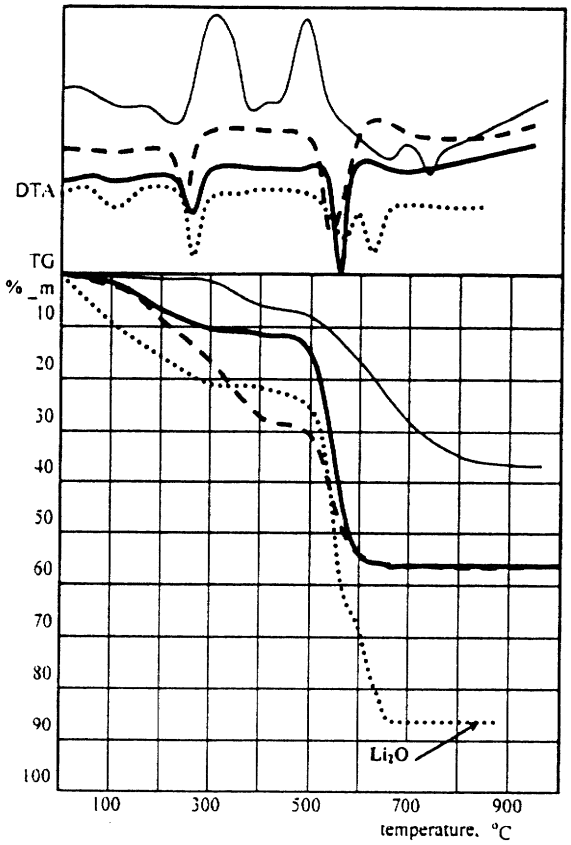

FIGURE 3
Thermal analyses of $LiNO_3$ (dotted line) and Li_2TiO_3 gels heated 48 h at 100°C: conventional (dashed line), ASCD (bold line), and with impregnated ASC (fine line)

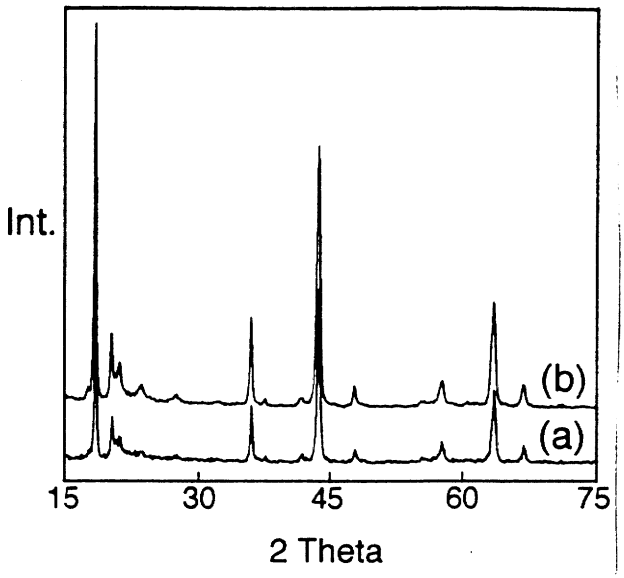

FIGURE 4
XRD patterns of Li_2TiO_3 powders obtained by heating gel at 800°C for 2 h: (a) conventional gel and (b) gel ASCD; the peaks are sharper in the latter gel

3.3 $BaTiO_3$

For preparation of barium titanates, a key was to maintain sols without precipitation of Ba nitrates. Thermal analysis of various gels prepared with addition of Ba nitrates and Ba hydroxide are shown in Fig. 7.

In all gels, two endotherms were observed. The first at ≈600°C can be attributed to melting; the second can be attributed to decomposition of Ba nitrates.

XRD patterns of $BaTiO_3$ gels heated to various temperatures are shown in Fig. 8. As was observed for the Li-containing gels, addition of ASC promoted formation of the desired crystalline phase. Nitrates were present at 500 to 570°C. At 600°C, all nitrates were decomposed over a 2 h period and formation of crystalline $BaTiO_3$ began. As observed for the Li titanates, this process was more advanced for the ASC-containing gels: the completely crystalline phase was formed after 24 h at 700°C. The temperature of formation and crystallization are comparable to what has been reported,[2-4,7,9,12,14] even when metalorganic reagents[28] were used.

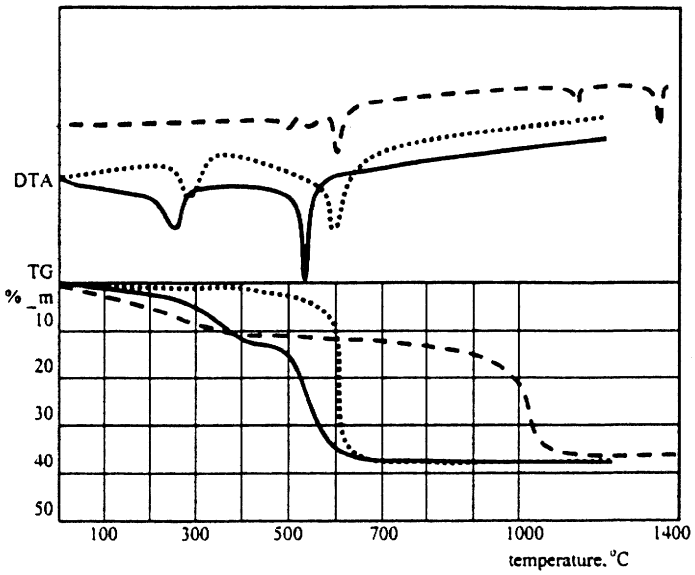

FIGURE 5
Thermal analysis of $Li_4Ti_5O_{12}$ heated 24 h at 200°C: conventional nitrate gel (dotted line), ASCD nitrate gel (bold line), and chloride gel (dashed line)

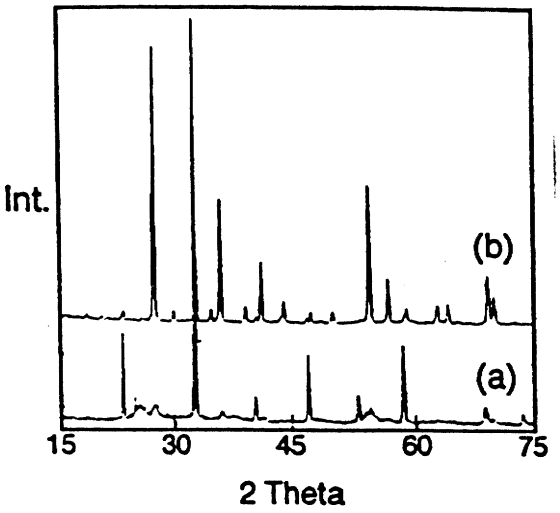

FIGURE 6
XRD patterns of fired nitrate $Li_4Ti_5O_{12}$ gels: (a) heated to 100°C and (b) heated to 600°C

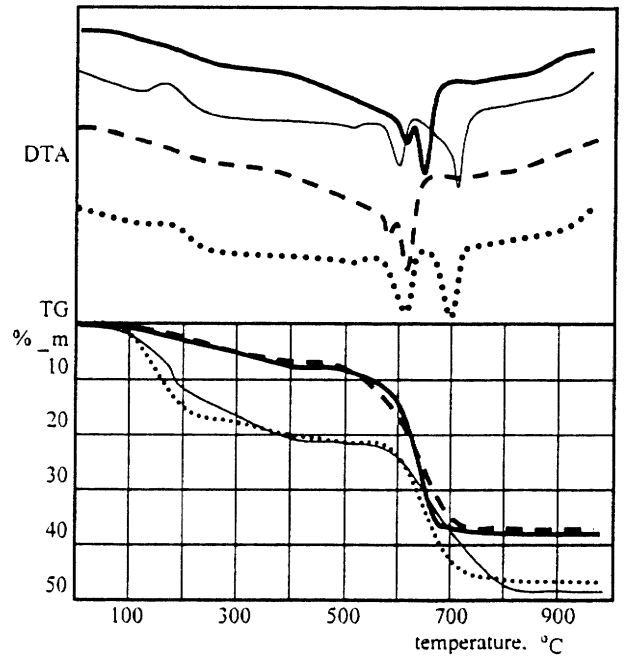

FIGURE 7
Thermal analysis of $BaTiO_3$ gels heated 20 h at 105°C: prepared with $Ba(OH)_2$ (conventional (bold line) and ASCD (fine line)); prepared with $Ba(NO_3)_2$ (conventional (dashed line) and ASCD (dotted line))

Following our success with production of medium-sized Li_2TiO_3 spherical particles, we prepared particles by a similar method from the Ba-Ti OH-NO_3 sol. We initially obtained Ba-Ti gel spheres of diameter 1-80 μm. However, we observed Ba loss and a final MR of Ba:Ti=0.2. Consequently, as in our former work,[28] we successfully impregnated the gels with $Ba(OH)_2$ in a hot solution (90°C, 25 g Ba/L), followed by vacuum drying, and final thermal treatment.

Following impregnation, we again obtained medium-sized spherical powders (Fig 9), which we have not been able to find in the literature. Such free-flowing powders should be useful in, for example, plasma-spraying techniques.[19,20] According our best knowledge, only fine (diameter < 1μm[5,23] and <10 μm[24]) $BaTiO_3$ particles have been obtained previously.

Thermal decomposition of the gels, before and after impregnation, yielded similar results (Fig. 10). An exotherm at ≈300°C may have indicated formation of the $BaTiO_3$ phase. During gelation in fresh ethylhexanol, nitrates appear to have been extracted (together with Ba^{2+}) by the solvent because melting and decomposition at ≈600°C were not observed.

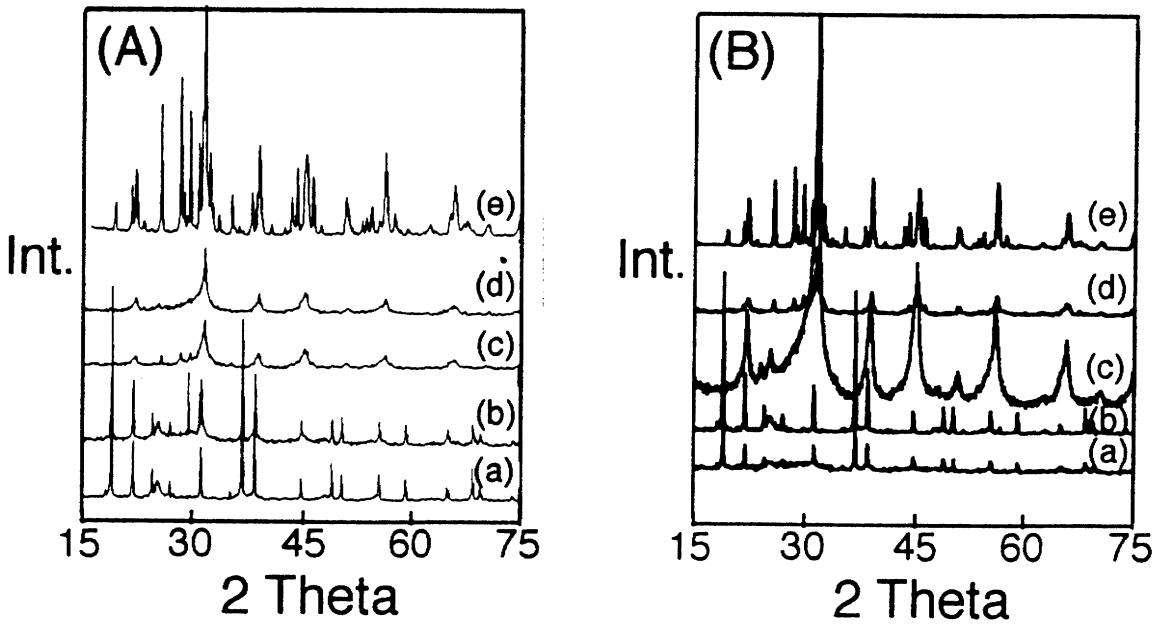

FIGURE 8
XRD patterns of $BaTiO_3$, (A) conventional gel and (B) ASC-containing gel, heated to: (a) 500, (b) 570, (c) 600, (d) 800, and (e) 1000°C.

4. CONCLUSIONS

We conclude the following:

1. Formation of stable concentrated Ti-nitrate sols (>170 g of Ti/cm^3) was favored by presence of ASC.
2. Gels prepared from stable, transparent Ti-nitrate sols, in which ASC was incorporated, formed crystalline titanate phases at lower temperatures than did gels without this additive.
3. In contrast to Li-Ti-OH-NO_3 sols, preparation of Ba-Ti-OH-NO_3 sols required special procedures because of limited solubility of Ba nitrate

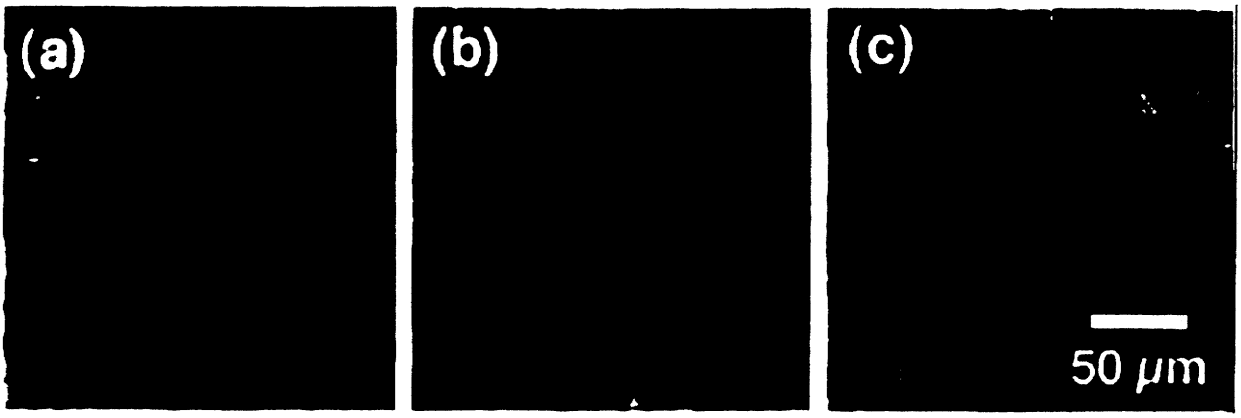

FIGURE 9
SEM photomicrographs of $BaTiO_3$ gels: (a) heated 20 h at 105°C, (b) and after impregnation with $Ba(OH)_2$ and heated under vacuum at 80°C for 15 min, and (c) impregnated gel and fired at 1000°C for 1 h

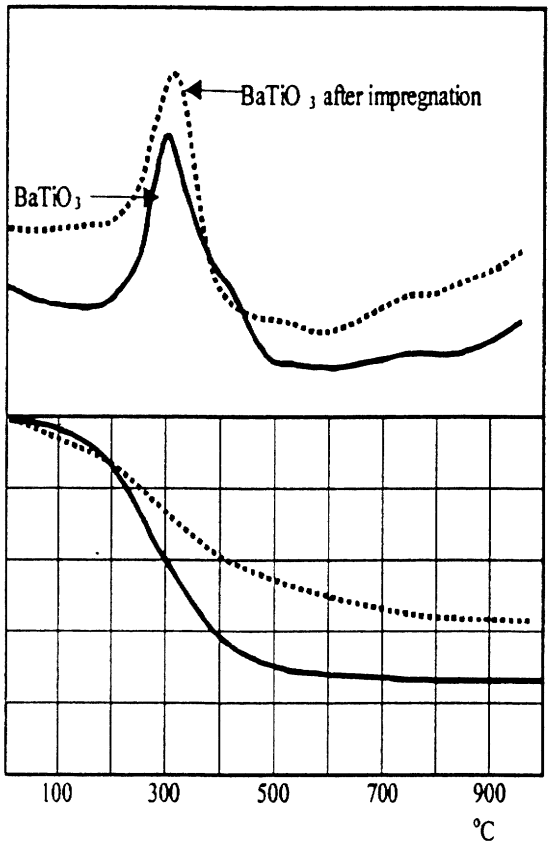

FIGURE 10
Thermal analyses of spherical $BaTiO_3$ gel particles before and after impregnation

4. Stoichiometry was maintained during preparation of irregularly shaped powders of titanates.
5. Correction of Me:Ti molar ratios during preparation of medium-sized spherical particles by emulsion-extraction process can be effected by impregnation with metal hydroxides.
6. No formation of metal carbonates was observed because of the very high acidity of the parent sols.
7. Formation crystalline phases was easier than for solid-state processes and comparable with other sol-gel techniques.

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